

Statistical Thermodynamics in Chemistry and Biology

9. Maxwell relations and mixtures

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Mathematics of partial derivatives

Today's agenda

- ▶ Design of fundamental equations
- ▶ Maxwell relations
- ▶ Homogeneous functions to develop the Gibbs-Duhem relationship
(The Gibbs-Duhem equation is not covered in the 2nd ed. of the book)

How to design a fundamental equation

- ▶ Each extensive degree of freedom in the fundamental equations is paired with its conjugate force. We already have: $\{p, V\}$, $\{T, S\}$, $\{\mu_j, N_j\}$.
- ▶ Other examples:
 - ▶ force, length - $f L$ - for elastic materials
 - ▶ surface tension, area - γA - for interfaces
 - ▶ electric potential, charge - ψQ - for charged particles
 - ▶ magnetic field, magnetic moment - $B I$ - for magnetic systems
- ▶ The fundamental equation for the **internal energy** becomes

$$dU = TdS - pdV + \sum_j \mu_j dN_j + f dL + \gamma dA + \psi dQ + B dI$$

U is special: all variables are extensive

- ▶ More general

$$dU = TdS - pdV + \sum_j \mu_j dN_j + \sum_j \mathcal{F}_j dX_j$$

where

$$\mathcal{F}_j = \left(\frac{\partial U}{\partial X_j} \right)_{S, V, N, X_{i \neq j}}$$

Surface tension

- ▶ When is it important? soap films, micelles, cell membranes, etc.
- ▶ System: γ is fixed and the area can change
- ▶ Choice of variables: T , p , N , and γ
- ▶ Begin by $U(S, V, N, A)$ (Nb! all extensive variables):

$$dU = TdS - pdV + \sum_j \mu_j dN_j + \gamma dA$$

- ▶ Change to (T, p, N, γ) :

$$-d(TS) + d(pV) - d(\gamma A) = -TdS - SdT + pdV + Vdp - \gamma dA - Ad\gamma$$

which gives

$$d(U - TS + pV - \gamma A) = -SdT + Vdp + \sum_j \mu_j dN_j - Ad\gamma = d(G - \gamma A)$$

- ▶ The system will be at equilibrium for (T, p, N, γ) when the thermodynamic function $G - \gamma A$ is at a minimum.

Ex. 9.2. Surface tension again

- ▶ Instead constant T , p , N , and A .
- ▶ The area is constant; the shape of the object will change (i.e. a drop on a surface)
- ▶ Again, begin by $U(S, V, N, A)$:

$$dU = TdS - pdV + \sum_j \mu_j dN_j + \gamma dA$$

- ▶ Change to (T, p, N, A) :

$$-d(TS) + d(pV) = -TdS - SdT + pdV + Vdp$$

which gives

$$d(U - TS + pV) = -SdT + Vdp + \sum_j \mu_j dN_j + \gamma dA = dG$$

- ▶ In this example we obtain the regular Gibbs free energy as the “minimum principle”.
- ▶ **Need to pay attention to the *independent variables*, in this case (T, p, N, A) .**

Maxwell relations: an example

- ▶ Use Euler's reciprocal relation, for example

$$\left(\frac{\partial^2 U}{\partial V \partial S} \right) = \left(\frac{\partial^2 U}{\partial S \partial V} \right)$$

- ▶ The fundamental equation for dU

$$dU = TdS - pdV + \sum_j \mu_j dN_j$$

- ▶ We thus have

$$T = \left(\frac{\partial U}{\partial S} \right)_{V,N} ; \quad p = - \left(\frac{\partial U}{\partial V} \right)_{S,N}$$

- ▶ Substituting this into Euler's relation gives:

$$\left(\frac{\partial T}{\partial V} \right)_{S,N} = - \left(\frac{\partial p}{\partial S} \right)_{V,N}$$

which is an example of a Maxwell relation.

How to obtain a Maxwell relation

- ▶ Suppose we for some reason are interested in obtaining

$$\left(\frac{\partial S}{\partial p}\right)_{T,N}$$

from the ideal gas law: $pV = Nk_B T$.

How to obtain a Maxwell relation

Part 2

1. Identify the **independent variables** and the corresponding **fundamental equation**: (use Table 8.1 or 9.1)

$$(p, T, N) \text{ and thereby } G(p, T, N)$$

2. Look at its differential form:

$$dG = -SdT + Vdp + \sum_{j=1}^m \mu_j dN_j$$

3. Construct **cross-derivates**:

$$-\left(\frac{\partial S}{\partial p}\right)_{T,N} = \left(\frac{\partial^2 G}{\partial p \partial T}\right); \quad \left(\frac{\partial V}{\partial T}\right)_{p,N} = \left(\frac{\partial^2 G}{\partial T \partial p}\right)$$

4. Euler's relation:

$$\left(\frac{\partial S}{\partial p}\right)_{T,N} = -\left(\frac{\partial V}{\partial T}\right)_{p,N} = -\frac{Nk_B}{p}$$

for an ideal gas.

Thermodynamics of a rubber band

Is the retraction in a rubber band driven by a change in enthalpy or in entropy?

- ▶ $U(S, V, L)$:

$$dU = TdS - pdV + fdL$$

- ▶ We are interested in enthalpy and entropy. Note that $dG = d(H - TS)$. So we get dG from $G(T, p, L)$:

$$dG = -SdT + Vdp + fdL$$

- ▶ The *force*, f , is given as

$$f = \left(\frac{\partial G}{\partial L} \right)_{T,p} = \left(\frac{\partial H}{\partial L} \right)_{T,p} - T \left(\frac{\partial S}{\partial L} \right)_{T,p}$$

- ▶ Since we can measure f , use Maxwell relations:

$$\left(\frac{\partial S}{\partial L} \right)_{T,p} = - \left(\frac{\partial f}{\partial T} \right)_{p,L}$$

i.e. the entropic contribution is obtained from measuring $f(T)$.

A rubber band

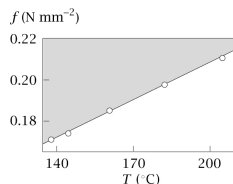
Part 2

- ▶ To get the enthalpy contribution, combine the two previous equations:

$$\left(\frac{\partial H}{\partial L}\right)_{T,p} = f - T \left(\frac{\partial f}{\partial T}\right)_{p,L}$$

which can be determined from the same experiment.

- ▶ Figure 9.1. shows that retraction of rubber increases with temperature (special property of rubber).
- ▶ The explanation is that the entropy decreases with length (also demonstrated in Ex. 2.4 where we studied the multiplicity of conformations with chain length).



Measuring expansion

- ▶ The **thermal expansion coefficient**, α , is defined as

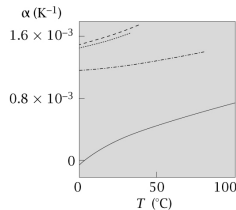
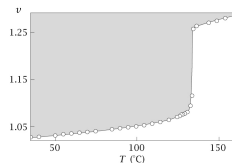
$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p$$

and is the fractional change in volume with temperature at constant pressure.

- ▶ For an ideal gas:

$$\alpha = \frac{p}{Nk_B T} \frac{Nk_B}{p} = \frac{1}{T}$$

- ▶ Upper figure: Specific volume v (volume/mass) of polyethylene.
- ▶ Lower figure: α for various liquids (water, benzene, etc.)



Measuring compression

- ▶ The **isothermal compressibility**, κ , is defined as

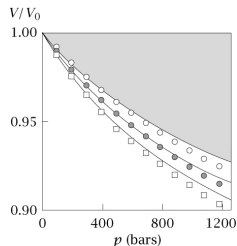
$$\kappa = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T$$

and is the fractional change in volume with pressure at constant temperature.

- ▶ For an ideal gas,

$$\kappa = \frac{1}{p}$$

- ▶ Graph: The relative volume, V/V_0 , of hexadecane. V_0 is the volume extrapolated to zero pressure.



Entropy change with pressure

- Consider the entropy change with pressure at constant temperature:

$$dS = \left(\frac{\partial S}{\partial p} \right)_{T,N} dp$$

- Combine the Maxwell relation

$$\left(\frac{\partial S}{\partial p} \right)_{T,N} = - \left(\frac{\partial V}{\partial T} \right)_{p,N}$$

with the definition of the thermal expansion coefficient, α ,

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_{p,N}$$

to get

$$dS = - \left(\frac{\partial V}{\partial T} \right)_{p,N} dp = -\alpha V dp$$

- α can be measured as a function of pressure:

$$\Delta S = - \int_{p_1}^{p_2} \alpha(p) V(p) dp$$

Partial molar volumes

Multicomponent systems have partial molar properties

- ▶ What is a **molar property**? For a system with n moles of a single component, the molar volume, $v = V/n$. Similarly, the molar Gibbs free energy, $g = G/n$.
- ▶ Multicomponent system in **mole**: $\mathbf{n} = n_1, n_2, \dots, n_m$. The **partial molar volume** is defined as,

$$v_j = \left(\frac{\partial V}{\partial n_j} \right)_{T, p, n_{i \neq j}}$$

- ▶ The change in volume, dV , is thus

$$dV = \sum_{j=1}^m \left(\frac{\partial V}{\partial n_j} \right)_{T, p, n_{i \neq j}} dn_j = \sum_{j=1}^m v_j dn_j$$

- ▶ In simple cases, v_j is independent of the composition and it can be obtained from the pure substance. In general, this is however not true. For an exercise, see *E9.1*.

The chemical potential

- ▶ The chemical potential is a partial molar free energy.
- ▶ We have for example

$$dU = TdS - pdV + \sum_{j=1}^m \mu_j dN_j$$

but we can also write

$$\mu_j = \left(\frac{\partial U}{\partial N_j} \right)_{S, V, N_{i \neq j}} = \left(\frac{\partial G}{\partial N_j} \right)_{T, p, N_{i \neq j}} = \left(\frac{\partial F}{\partial N_j} \right)_{T, V, N_{i \neq j}} = \left(\frac{\partial H}{\partial N_j} \right)_{S, p, N_{i \neq j}}$$

- ▶ Partial molar quantities are defined *specifically* for quantities at **constant T and p** . So only the Gibbs free energy

$$\mu_j = \left(\frac{\partial G}{\partial N_j} \right)_{T, p, N_{i \neq j}} = \left(\frac{\partial H}{\partial N_j} \right)_{T, p, N_{i \neq j}} - T \left(\frac{\partial S}{\partial N_j} \right)_{T, p, N_{i \neq j}} = h_j - Ts_j$$

is called a **partial molar quantity**.

Partial molar properties are linked

- ▶ We have from the definition of the partial molar volume:

$$dV = \sum_{j=1}^m v_j dn_j$$

- ▶ In general,

$$V = \sum_{j=1}^m v_j n_j$$

thus also in general

$$dV = \sum_{j=1}^m (v_j dn_j + n_j dv_j)$$

which leads to

$$\sum_{j=1}^m n_j dv_j = 0$$

- ▶ It shows that the partial molar volumes are not independent of each other.

The Gibbs-Duhem equation

Same procedure again...

- ▶ Consider $U(S, V, N)$,

$$U = TS - pV + \sum_{j=1}^m \mu_j N_j$$

- ▶ Differentiate,

$$dU = TdS + SdT - pdV - Vdp + \sum_{j=1}^m \mu_j dN_j + \sum_{j=1}^m N_j d\mu_j$$

- ▶ Subtract the fundamental equation for U ,

$$dU = TdS - pdV + \sum_{j=1}^m \mu_j dN_j$$

The Gibbs-Duhem equation

Part 2

- ▶ This gives the **Gibbs-Duhem** equation.

$$\sum_{j=1}^m N_j d\mu_j = Vdp - SdT$$

and at constant temperature and pressure,

$$\sum_{j=1}^m N_j d\mu_j = 0$$

- ▶ Central for example for understanding phase transitions.

Summary

- ▶ Design fundamental thermodynamic functions from a set of independent variables.
- ▶ Maxwell relations - provides a way to obtain unmeasurable properties from measurable ones. List of Maxwell relations: See Table 9.1
- ▶ Multicomponent systems - The Gibbs-Duhem equation (and similar expressions).

Exam Aug. 2011 - Exercise 1

Maxwell relations

- a) Describe in a few sentences what a Maxwell relation is. What is the theoretical (mathematical) foundation used to derive Maxwell relations from a fundamental equation? Why are they useful, for example in experimental work?
- b) For a single-component system where each particle has a charge, q , give the fundamental equation for the Helmholtz free energy for a system in an external electrostatic potential, ψ . Give the Maxwell relations for this fundamental equation which includes ψ .
- c) Show the following relation (where we in this derivation assume that $dq = Ze dN$):

$$\left(\frac{\partial U}{\partial N}\right)_{T,V} = (\mu + Ze\psi) - T \left(\frac{\partial \mu}{\partial T}\right)_{V,N} - ZeT \left(\frac{\partial \psi}{\partial T}\right)_{V,N}$$